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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Primary to secondary organic aerosol: evolution of organic emissions from mobile combustion sources" *by* A. A. Presto et al.

Anonymous Referee #1

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This manuscript discusses a chamber study on the transformation of POA and the photochemical formation of SOA in dilute vehicle exhaust. PMF was performed to the organic aerosol data acquired with a Q-AMS to determine the time series and mass spectra of SOA and POA. 2-factor solutions were used. Based on these results, the authors discussed the evolution of OA and the mixing behavior of POA and SOA during photo-oxidation. The oxidation mechanism was also examined using the Van Kravelen diagram and the f44-f43 triangle plot. This study provides information that is important for understanding the evolution of organic emissions from mobile combustion sources. The contents are suitable for publication in ACP. I recommend acceptance for

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Interactive Discussion
Discussion Paper

publication after the authors respond to the following comments.

The discussion about the mixing behavior of POA and SOA seems a bit overreached. The wall loss corrected POA time trend shown in Fig 6 is very noisy. Were the POA increases during the 1st hour statistically significant? What's the performance of the model for predicting SOA formation? In terms of wall loss correction, how was black carbon measured, what are the measurement uncertainties? It might be useful to provide error estimates for the wall-corrected POA data.

Some thermodenuder data are shown in Fig. 1, but no additional information is given. Nothing is known about TD temperature, residence time, etc. According to the TD data, roughly $\frac{1}{4}$ of the POA remained under heating (Fig 1). Yet, POA was found to evaporate completely according to some experiments. Are these results consistent?

Was the residual shown in Fig. 1b the simple sum of the residuals at all m/z's? If so, the small values may not necessarily indicate good fit; they could arise simply because of the cancelling effect of adding up positive and negative values. It may be more appropriate to show the sum of the absolute values of the residuals or show the Q/Qexp time trend. In fact, I recommend the authors provide the diagnostic plots for the PMF work performed in this study. The m/z 44 signal in the D4 POA factor appears too high to be realistic. Is it possible that gas phase CO2 subtraction was not done perfectly? It is particularly suspicious since the rest of the D4 MS after excluding m/z 44 and 18 peaks look very similar to the normal-looking POA MS.

The SOA spectra extracted from PMF in this study looks more different than ambient SOA spectra. But the SOA spectra of vehicle exhaust reported in Sage et al. based on an earlier work conducted in the same group are more similar to ambient SOA. Sage et al. also found the SOA MS in vehicle exhaust changed over the course of photo-oxidation, yet this study used PMF to extract the SOA spectrum, thus assumed that the SOA spectrum is fixed over time. The issue whether the SOA spectrum is indeed constant over time should be more thoroughly investigated. Was the approach

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of Sage et al. applied to the data of this study? Since Sage et al. assigned all m/z 57 to POA, which may not be valid, another approach to check this issue is to examine the difference matrix:

diff_mx = mx_org – mx_POA = mx_SOA + mx_residual

This will allow the variations in the MS of SOA be examined, assuming the POA spectrum is constant.

Detailed comments:

Last paragraph, P24266, placing the in-text citations after "," is confusing.

P24270, 2nd paragraph, why heat to 47 C? What's the significance of this temperature?

P24270, L21, how much of the mass is BC?

P24271, L18, in addition to citing the paper, it is necessary to briefly describe the method used to apportion the nitrate signal.

Fig1, why does the blue dashed line start around -1? Wall losses should be happening all the time when there are particles in the chamber.

P24275, 2nd paragraph, the discussion of quantification limit needs clarification. How was the quantifiable limit determined, under what experimental condition? What's the averaging time for the quoted 0.3-0.5 value? The observation of 0.3 ugm-3 background OA signal in filtered air could be an indication that the AMS fragmentation table was not adjusted properly. Has this issue been examined closely? What does the mass spectrum of this background signal look like? Does it look like the MS of the SOA factor? If not, what's the base of estimating the detection limit of SOA according to this value? As shown in Fig. 1, small SOA signals began to appear at t = -0.5h, but the signal was zero earlier. If SOA is not expected to occur before t=0, have the authors tried to use fpeak to tune away the SOA signal before t =0?

P24275, 3rd paragraph, it is strange that a 7% reduction of Q/Qexp led to almost no

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change in the residuals. It may be worthwhile to show in the supplementary material some PMF diagnostic plots. Showing the results from factor 3 may also be useful to compare with the 2 factor solution.

P24275, line 27, “reduced peak” is vague. Please revise.

P24277, L9, it is said “The number of PMF factors determined by Craven et al. is broadly consistent with the PMF analysis presented here..” What is consistent, the factor spectra? Fig. 4, how do the SOA spectra look like?

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 24263, 2013.